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Corrosion Behavior of Nickel Alloys in Wet Hydrofluoric Acid

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Hydrofluoric acid is a water solution of hydrogen fluoride (HF). Hydrofluoric acid is used widely in diverse types of industrial applications; traditionally, it is used in pickling solutions in the metal industry, in the fabrication of chlorofluorocarbon compounds, as an alkylation agent for gasoline and as an etching agent in the industry of glass. In recent years, hydrofluoric acid has extensively been used in the manufacture of semiconductors and microelectronics during the wet chemical cleaning of silicon wafers. Hydrofluoric acid can be considered a reducing acid and although it is chemically classified as weaker than, for example, sulfuric or hydrochloric acids, it is extremely corrosive. This acid is also particularly toxic and poses greater health hazard than most other acids. The corrosion behavior of metals in hydrofluoric acid has not been as systematic studied in the laboratory as for other common inorganic acids. This is largely because tests using hydrofluoric acid cannot be run in standard equipment and because of the toxic nature of this acid. Moreover, short-term weight loss laboratory corrosion tests in hydrofluoric acid can be frustrating since the results are not as highly reproducible as in the case of other acids such as sulfuric or hydrochloric. One of the reasons is because hydrofluoric acid commonly attacks the coupons used for testing in a non-uniform manner. That is, the corrosive power of this acid is not aimed to uniform thinning but mostly to localized penetration below the skin of the metal in the form of thin cracks, voids, pits, trenches and sometimes intergranular attack. Figure 1 shows the cross section of a coupon of Alloy 600 (N06600) exposed for 336 h to the vapor phase of a solution of 20% HF at 93°C. In cases where internal penetration occurs such as in Figure 1, it may not be recommended to use corrosion rates based on weight loss for material selection.

The choices of engineering alloys to handle hydrofluoric acid are limited. Some non-metallic materials such as polyethylene can be used. However, traditional materials such as glass and the reactive metals such as titanium, zirconium and tantalum are readily attacked by hydrofluoric acid. Hydrofluoric acid will dissolve most oxides and therefore any alloy that may rely on a passive oxide film for protection against corrosion will not perform well in presence of this acid. Hydrofluoric acid at concentrations higher than 64% can be handled with carbon steel; however, at lower concentrations, this acid attacks the steel rapidly. [1,2] Steels also may suffer embrittlement in presence of hydrofluoric acid. [2] Since nickel alloys offer moderate corrosion resistance over a wide range of acid concentration and temperature, they are a common choice for wet hydrofluoric acid. [3-9] For example, it has been reported that in solutions containing mixtures of hydrofluoric and nitric acids, a high chromium nickel alloy such as G-30 (N06030) performed well. [4] The most popular traditional metal used for hydrofluoric acid is the Ni-40% Cu alloy 400, (N04400) even though its corrosion resistance is greatly diminished by the presence of air or oxidizing salts. [1-3, 5-9] Another nickel alloy containing only 1.6% Cu (N06200) was also shown to perform well in hydrofluoric acid. [9] It has been reported in the literature that the resistance to corrosion of engineering alloys in wet HF service was a consequence of the formation of insoluble fluoride salts on the surface of these alloys. [1,2,5]

The two most promising alloys for hydrofluoric acid applications seem to be C-2000 (N06200) and 400 (N04400). The corrosion behavior of these two nickel alloys in hydrofluoric acid has been characterized regarding the effect of temperature, acid concentration and testing time. [9] Table 1 (adapted from Reference 9) shows the corrosion rate by weight loss and the depth of attack by internal penetration as a function of the temperature and vapor vs. liquid phase of exposure for a testing time of 240 h. As the testing time increased from 24 h to 240 h, the corrosion rate of N06200 in the vapor phase or 20% HF both at 79°C and 93°C markedly decreased, while in the liquid phase the corrosion rate was almost independent of the testing time. [9] On the other hand, under the same testing conditions, the corrosion rate of N04400 in the liquid phase slowly increased as the testing time increased. In the vapor phase, the corrosion rate of N04400 was high (100-400 mpy) and independent of the testing time. [9] As it could be

expected, as the acid concentration increased from 1% to 20% the corrosion rate of both N06200 and N04400 increased; however the effect was more pronounced for N04400, especially in the vapor phase. [9] Both N06200 and N04400 had similar corrosion rates at the lower temperatures of 38°C and 52°C; however as the temperature was raised to higher values (e.g. 79°C and 93°C) the corrosion rate of N04400 increased faster than the corrosion rate of N06200 both in the vapor and liquid phases (Table 1). [9] Table 1 also shows that the internal penetration in N04400 was high at all temperatures in the vapor phase. On the other hand, in the liquid phase the internal penetration was higher for N06200, mainly at 79°C and 93°C. [9]

Other nickel alloys containing just molybdenum (such as N10675) and iron (such as N06600 and N06030) do not perform as well as N06200 or N04400 in this acid. Chromium seems to be a beneficial alloying element for vapor phase applications. [9] It is apparent that copper is the most beneficial alloying element for nickel alloys while iron seems to be detrimental. [9]

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REFERENCES

1. M. G. Fontana “Corrosion Engineering” 3rd Ed., p. 353 (McGraw-Hill, New York, 1986)
2. T. F. Degnan, Process Industry Corrosion -The Theory and Practice, p. 275-282, (NACE International, 1986).
3. NACE International publication 5A171 “Materials for Receiving, Handling and Storing Hydrofluoric Acid” (NACE International, 1995).
4. E.-M. Horn, P. E. Manning and M. Renner, Werkstoffe und Korrosion, 43, 191-200 (1992).
5. S. W. Ciaraldi, R. M. Berry and J. M. Johnson, Corrosion/82, Paper 98, (NACE International, 1982).
6. S. J. Pawel, Corrosion, 50, 963-971 (1994).
7. C. M. Schillmoller, Chem. Eng. Progress, pp. 49-54, November 1998.
8. J. R. Crum, G. D. Smith, M. J. McNallan and S. Hirnyj, Corrosion/99, Paper 382 (NACE International, 1999).
9. R. B. Rebak, J. R. Dillman, P. Crook and C. V. V. Shawber, Materials and Corrosion, 52, 289-297 (2001).

TABLE 1
Effect of Temperature on the Corrosion Behavior of Unstressed coupons.
Alloys 400 and C-2000 exposed in 20% HF for 240 h. (From Reference 9)

Alloy	T (°C)	Exp.	Average Corrosion Rate by Weight Loss in mpy (mm/year)	Rolled face Internal Penetration in mils (µm).	Observations in the corroded coupons
400	38	L	10.5 (0.27)	0.5 (13)	Uniform corrosion, (A)
400	38	V	45.15 (1.15)	9.5 (241)	IGA. Cracks at the perforated hole and edges.
400	52	L	18.05 (0.46)	0.5 (13)	Uniform corrosion, (A) GB etching
400	52	V	130.5 (3.31)	24.5 (622)	Severe IGA, Some cracks from edges
400	66	L	8.5 (0.22)	0.5 (13)	Uniform corrosion, (A)
400	66	V	69.45 (1.76)	7.5 (191)	IGA. Cracks along drilled hole.
400	79	L	43.35 (1.10)	1 (25)	Uneven corrosion, GB etching.
400	79	V	299 (7.59)	14 (356)	Deep IGA
400	93	L	80.95 (2.06)	1 (25)	Uneven corrosion. GB etching
400	93	V	483.5 (12.3)	14.5 (368)	Deep IGA and uneven corrosion.
C-2000	38	L	8.3 (0.21)	0.5 (13)	Uniform corrosion, (A)
C-2000	38	V	7.55 (0.19)	9.5 (241)	Uniform corrosion, (A), Trace of Cu on surface.
C-2000	52	L	18.8 (0.48)	0.5 (13)	Uniform corrosion, (A), Cu on surface.
C-2000	52	V	14.35 (0.36)	0.5 (13)	Uniform corrosion, (A)
C-2000	66	L	33.5 (0.85)	1.5 (38)	Uneven general corrosion, Small dealloyed layer. Sample plated with Cu and probably Ni.
C-2000	66	V	33.45 (0.85)	0.5 (13)	Minimal corrosion. Sample plated with Ni and traces of Cu
C-2000	79	L	26.25 (0.67)	4 (102)	Thin lace-like penetration. Light Cu color.
C-2000	79	V	36.1 (0.92)	1.5 (38)	Shallow isolated lace-like penetration
C-2000	93	L	29.25 (0.74)	8.5 (216)	Thin lace-like penetration
C-2000	93	V	27.3 (0.69)	2.5 (64)	Isolated lace-like penetration, Green corrosion products.

(A) = Roughness Reported as Internal Penetration, IGA = Intergranular Attack, GB = Grain Boundary,

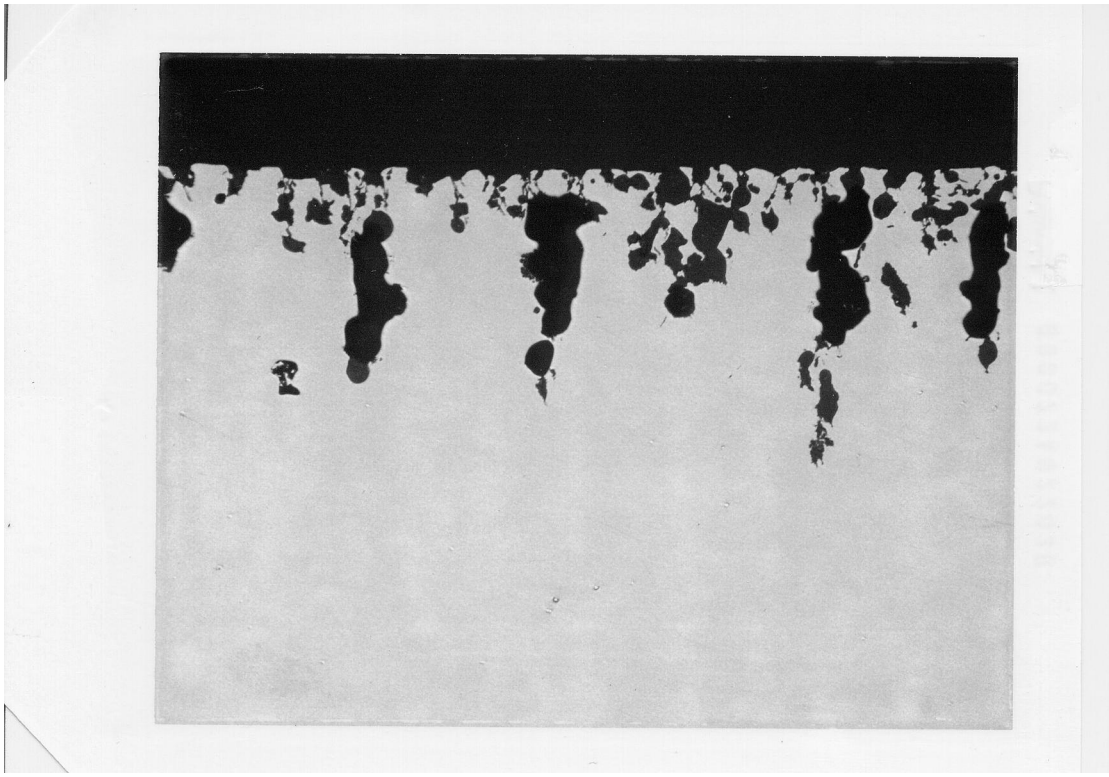

FIGURE 1: Specimen of Alloy 600 (N06600) exposed for 336 h to the vapor phase of 20% HF solution at 93°C. Magnification X100.